1999 Annual Report

RESEARCH AND DEVELOPMENT

Ontario

Laboratory Services Branch
Ontario Ministry of the Environment
March, 2000

1999 Annual Report
Research and Development
Laboratory Services Branch
March 2000

March 2000

Cette publication technique
n'est disponible qu'en anglais.

Printed on 50% recycled paper
including 10% post-consumer fibre

ISSN 1203-0104

PIBS 2511e07

Overview

Over the past year, Laboratory Services Branch (LSB) staff have emphasized the completion of several projects started over one year ago, rather than introducing many new projects. Key new methods such as the dioxin-like PCBs – which were requested by several LSB customers – have now been brought on-line. New methods have also been introduced to take advantage of the capabilities of liquid chromatography-mass spectrometry (LC/MS), as several new methods based on LC/MS were introduced. Overall, the LSB R&D effort was reduced compared to the previous few years, which simply reflects an overall reduction of resources available for this function. It is expected that the resources available for R&D may fluctuate over the next few years, as the LSB consolidates and clarifies its roles both as a reference centre, and as an analytical service supplier for other MOE programs.

One reference centre activity that has continued to grow is the LSB Seminar Series. Several seminars were a result of LSB-commercial sector partnerships, which were sometimes advertised widely by the commercial partner. As a result, attendance at seminars has been high, and more people from outside MOE have attended. We expect interest in the seminars will grow, as they are an excellent and inexpensive vehicle for keeping up-to-date concerning developments in the environmental analytical field. Anyone who wishes to be notified of future seminars should contact Ray Clement.

For further information on any of the projects or activities described in this report, readers are directed to the Study Leader, or to the Author:

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A. New Applications of Technology

Introduction

In the past year, liquid chromatography/mass spectrometry (LC/MS) has started its transformation from a novel technology to a routine analysis tool, as work on the use of LC/MS for selected pesticides have resulted in the completion of two new methods. The maturation of the LC/MS technology also gives the Ministry of Environment valuable new tools to study high molecular weight and polar compounds that previously were not readily amenable to conventional gas chromatography-mass spectrometry analysis. In collaborative work with a leading instrument manufacturer, an even newer technology – liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS) – was used to produce impressive results for a difficult environmental analysis application. It seems that the combination of liquid chromatography with various forms of mass spectrometry is going to be an important area of research for environmental analysis applications over the next 5-10 years.

Work also continued on the use of Inductively-Coupled Plasma Mass Spectrometry (ICP/MS) for metals determination in complex samples, in this case – fish samples. The use of ICP and ICP/MS technologies for environmental applications has grown world-wide to the point where methods based on these technologies are clearly the methods of choice for rapid, multi element analyses.

I. LC/MS Determination of Glyphosate and Aminomethylphosphonic Acid

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Bick Nguyen & Paul Yang
Customer:	Environmental Monitoring and Reporting Branch (Pat Lachmaniuk)

Objective

To develop a high sensitivity, liquid chromatography separation, electrospray ionisation mass spectrometry (LC/MS) analytical method for the analyses of glyphosate (Round Up) and its metabolite aminomethylphosphonic acid (AMPA), one the most commonly used herbicides in Southern Ontario. A method for the analysis of these target substances in sample sample types such as water, and vegetation, with good recovery, high sensitivity, and consistency across all sample types is required to support the Pesticide Act of Ontario (PAO).

Background

The driving forces of this project are:

- The Operation Division (OD) of the Ontario Ministry of the Environment requires an analytical method for the analysis of glyphosate in various environmental sample types such as water and vegetation

- Staff of the OD require methods for the enforcement of the PAO; hence, the ability to produce consistent analytical data in various aqueous sample types, with good recoveries and superior sensitivity when operated in the presence/absence analysis mode is needed.

Results

A new procedure has been devised for multimedia sample preparation for LC/MS analysis. An LC/MS method has been completed for the analysis of glyphosate and its metabolite aminomethlyphosphonic acid (AMPA) in environmental waters and vegetation samples. The method used isotopic dilution for quantification of glyphosate

and external standard determination of AMPA. Method detection and recovery are shown in the following table.

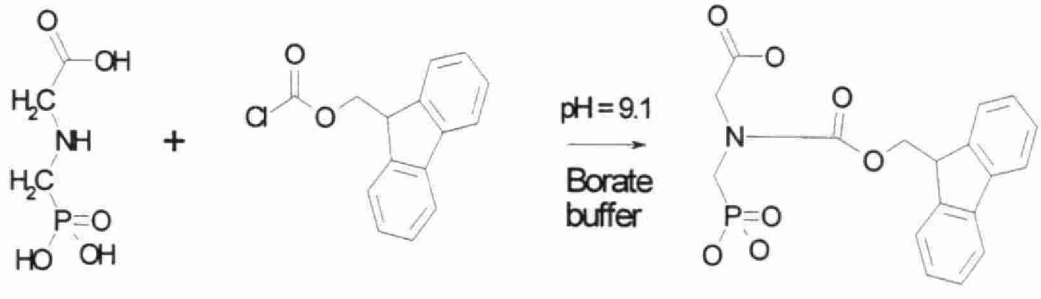
		Glyphosate	AMPA
Method MDL	Water	7.0 µg/L	15 µg/L
	Vegetation	0.7 µg/g	0.2 µg/g
Method W value	Water	2.0 µg/L	5.0 µg/L
	Vegetation	0.2 µg/g	0.2 µg/g
Average recovery	Water	96±12 %	99±25 %
	Vegetation	80±13 %	66±12 %

Current Status

Glyphosate: The glyphosate method, developed for water and vegetation samples, is completed and on-line (Method E3415).

Principle of the method. The method is developed for the detection of glyphosate and its metabolite aminomethylphosphonic acid (AMPA). The analysis is performed by HPLC , with electrospray ionisation and MS detection, based on the determination of the 9-fluorenyl methoxycarbonyl chloride (FMOC-Cl derivatives of glyphosate and AMPA. A schematic of the reaction is shown below.

Reaction of glyphosate with FMOC-Cl



Glyphosate (MW = 169) FMOC-Cl FMOC-Gly (MW = 391)

The retention of the highly polar glyphosate ion on the reversed phase HPLC column is minimal. The retention of the derivative however, is greatly enhanced allowing for quantitative analysis of the analytes. The preparation of water samples involve evaporating an aliquot of sample to dryness before reaction with the FMOC-Cl in the presence of a borate (pH 9) buffer. No sample cleanup is required prior to analysis. A six week storage study was performed on glyphosate water samples, and results to date show that aqueous samples may be stored for up to six weeks at 4±2° C without appreciable deterioration of glyphosate.

Vegetation samples are extracted with a neutral water:dichloromethane mixture followed by cleanup using Bio-Rad AG 50W-X8 resin (H^+ form) prior to reaction with the FMOC-Cl. The reaction process is identical to that of the water samples. Sample preparation is followed by HPLC-MS analysis using an internal standard method. The internal standard $^{13}C_2$ ^{15}N-glyphosate is added to the original sample aliquots prior to all sample preparation procedures. Retention times of FMOC-Gly and AMPA may shift depending upon the species of the plant and origin of samples. Therefore, standard addition of glyphosate into the final sample extract may be used for further confirmation of the identification of glyphosate in vegetation samples.

II. LC/MS Determination of Diquat and Paraquat in Environmental Samples

Study Leader:	Lorna Grey, Applied Chromatography Section
Study Team:	Bick Nguyen & Paul Yang
Customer:	Operation Division, Pesticide Analysis Lead (Gary Martin)

Objective

To develop a high sensitivity liquid chromatography separation, electrospray ionisation – (isotope dilution) mass spectrometry (LC/ESI-IDMS) analytical method for the analysis of paraquat and diquat herbicides in environmental samples such as water and vegetation, and solid sample types to support the Pesticide Act of Ontario (PAO).

Background

The Operation Division of the Ontario Ministry of the Environment requires an analytical method for the determination of diquat and paraquat herbicides in various environmental sample types. The ideal method will have the ability to produce consistent multi-media analytical data with superior recoveries, high accuracy, and the highest sensitivity possible when operated in the presence/absence analysis mode, thereby providing an effective tool for the enforcement of the PAO. The enforcement aspect is especially important during the spraying of these herbicides, as cross-boundary pesticide drift is a common occurrence.

Results

Based on the original LSB method E3404, a new method has been developed for the required Data Quality Objectives (DQO) as indicated by Customers. Validation of the new method, and the development of a new solid phase extraction procedure that can be used for the preparation of multi-media samples, have been completed. A 2-month field study, which involved the analysis of 207 water samples, was carried out to determine sample stability, the need for sample preservatives, and storage conditions and times. Also included in the method was an extensive study which validated, for the first time, that typical recoveries of native and isotopic-labelled (via deuterium) diquat and paraquat are statistically equal. This eliminated prior concerns about [H⇔D] exchanges under these sample preparation conditions and justified the use of isotopic dilution for this application.

Current Status

The PQDQ method is on-line (Method E3417). It was completed as an External Standard Method and not the Isotope Dilution method that was originally intended. Lorna Grey presented the results of this method at the 31st Eastern Canada Pesticide and Environmental Contaminants Workshop, May 18, 1999 in Niagara-on-the-Lake, Ontario.

III. LC-(Electrospray Ionisation) MS Determination of Microcystins

Study Leader :	Steve Jenkins, Mass Spectrometry Section
Study Team :	Vince Taguchi
Customer :	Environmental Monitoring and Reporting Branch, Standards Development Branch

Objectives

To develop a quantitative analytical method for microcystins in drinking water by Liquid Chromatography - (Electrospray Ionisation) Mass Spectrometry [LC-(ESI)MS].

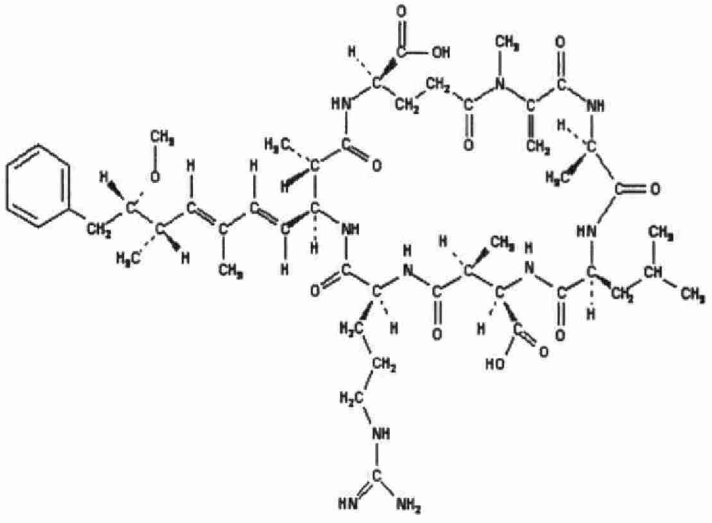
Background

Microcystins are cyclic heptapeptide hepatotoxins produced by cyanobacteria (blue-green algae; see structure below). Genera known to produce toxins include *Microcystis*, *Oscillatoria*, *Aphinizomenon*, *Anabaena* and *Nostoc*. So far, more than 50 microcystins have been identified. Microcystins have been responsible for the poisoning of fish, birds and animals in many countries. In 1996, over 40 patients undergoing dialysis treatment, in the Brazilian city of Caruaru, died from microcystin poisoning from contaminated water. Microcystins have also been found to be tumour promoters. The most toxic and most abundant congener is microcystin-LR. The intracellular toxins are released at the later stages of the cell's life cycle or when water is treated with an algicide which lyses the cell wall. The toxicity of microcystin-LR is related to its irreversible inhibition of the protein phosphatases 1, and 2A.

Results

Previously, a procedure was developed for the analysis of soluble microcystin-LR in drinking water using C18 SPE disks. However, it was discovered that the toxin could be extracted from water using bulk C18 SPE material. This made the method less costly as well as more reproducible. The microcystin-LR is quantitated against the internal standard Gramicidin S (a cyclic decapeptide antibiotic). The detection limit with the bulk C18 SPE material remained the same as before, approximately one order of magnitude below the proposed drinking water guideline of 1.5 µg/L.

Microcystin-LR



Current Status

The microcystins are mass analysed at low resolution (1000 RP) on a tandem hybrid mass spectrometer to make the method transferable to low resolution (quadrupole or ion trap) mass spectrometers. This increases the possibility of detecting interferences, although no interferences have been detected so far in the limited number of samples analysed. High resolution mass spectrometry may be used if found to be necessary. The inclusion of four microcystins in the same analytical run has significantly increased the chromatographic run time as a set of samples takes 2 to 3 days of instrument time.

The present method only analyses for extracellular soluble microcystin-LR. The chromatographic separation and mass spectrometric detection of other microcystins, -RR, -YR and -LA (those that are commercially available as standards) have been developed. Standards of the microcystins -LF and -LW have also been recently obtained and may be incorporated into the method. Further development work will involve the analysis of intracellular microcystins in order to determine the toxic potential of blooms. The current method still requires an improvement in precision and accuracy for the added compounds.

IV. ICP-MS Analysis of Fish Tissue for Trace Metals

Study Leader :	Mark Powell, Spectroscopy Section
Study Team:	Nada Gnanalingham, Lorraine Peters, Peter Grauds
Customer :	Eastern Region - Operations Division

Objectives

To develop a new analytical method for trace metals in fish tissue to support studies in the Moira River Project. The trace metal data will be used in conjunction with other types of analysis to provide the public with information on health risk and to assess the existing impact of pollution caused by mining operations on the Moira River system.

Background

The Moira River is still being contaminated with arsenic (As), copper (Cu) and cobalt (Co) originating from the Deloro Mine site at the town of Deloro. Elevated levels of arsenic have been found in sediment in Moira and Stoco Lakes and at the mouth of the river in the Bay of Quinte. Due to recent health concerns and the possibility of a site cleanup, an impact study of the environmental state of the Moira River has been implemented. Golder Associates have been contracted by the MOE Eastern Region to co-ordinate this study and report on findings by March 2000. An important part of this study is to ascertain the effects of trace metal contamination in a variety of sample types including fish tissue. LSB has historical expertise in the area of trace metal analysis and was requested by the Eastern Region and the Moira River steering committee to supply Golder Associates with fish analysis data.

Analysis of samples for trace elements including aluminum (Al), cobalt (Co), copper (Cu), nickel (Ni), zinc (Zn), arsenic (As), silver (Ag), lead (Pb), mercury (Hg) and uranium (U) was requested. Conventional methods using atomic adsorption at LSB exist for some of the above analytes, but not all. In addition, lower detection limits were required. ICP-MS was chosen as the technology for a new method for all the above parameters with the exception of mercury which was done by the conventional method of cold vapour AA.

Results

Successful whole fish analysis of white suckers and long nose dace for trace metals using ICP-MS was conducted and results have been forwarded to Golder Associates which will be presented in their final report. An oral presentation describing the method development was presented at the FACSS conference at Vancouver, BC in October 1999.

Current Status

A new method for fish tissue analysis has been developed (Method E3416) and a method development report and standard method write up completed. This method was developed specifically for this study. However, the method could be used to support additional studies including the sport fish analysis program co-ordinated by the Environmental Monitoring and Reporting Branch.

V. LC-MS/MS Methods for Nonylphenol and Nonylphenol Ethoxylates

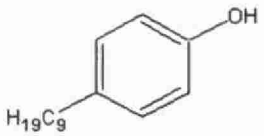
Study Leader :	Patrick Crozier and Vince Taguchi, Mass Spectrometry Section
Collaborators :	Jeff Plomley and Yves Mouget (MDS Sciex)
Customer :	Ian Smith, Water Policy Branch; R. Kettry, Canada Ontario Agreement (COA), STP Characterization

Objectives

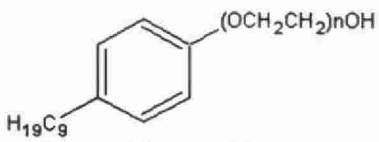
To develop selective and sensitive mass spectrometry methods for the quantitative determination of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) in a variety of sample types; to use LC-MS/MS and GC-MS/MS methods for the testing of sewage treatment plant (STP) samples to establish baseline levels of NP and NPEs in wastewater. The new methods will complement the existing LSB qualitative GC-MS characterization method.

Background

NPEs are non-ionic surfactants utilized in domestic and industrial cleaners as well as in the textile and pulp and paper industries. Because they are a component of various cleaners, NPEs have been detected in various wastewater streams including STPs. NPEs are of environmental concern because of their tendency to degrade to NP; NP and the lower molecular weight NPE congeners are members of a group of chemicals known as *endocrine disruptors* – thought to cause growth and reproductive problems in biota. Several Ontario municipal sewer use bylaws have tentatively included NP and NPEs.



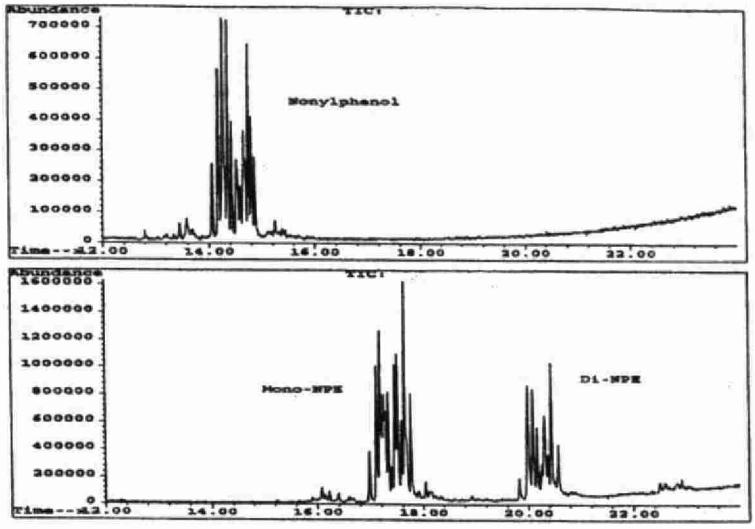
4-Nonylphenol



4-Nonylphenol Ethoxylate

The requirement for low detection limits and compound specificity coupled with the high chemical backgrounds in complex environmental samples make mass spectrometry the preferred tool for NP/NPEs determination. GC-MS techniques are adequate for detecting NP and lower molecular weight NPEs homologues (< $[EtO]_5$). LC-MS is amenable to the analysis of the higher molecular weight NPEs homologues ($[EtO]_{1-20}$) but lacks the chromatographic resolution to separate individual isomers/congeners of the congener groups. Tandem mass spectrometric techniques (LC-MS/MS and GC-MS/MS), which offer an inherent degree of selectivity (via precursor ion isolation) and specificity (precursor ion fragmentation to form a product ion spectrum fingerprint), were explored as a means of eliminating matrix interferences while maintaining sensitivity. Multiple reaction monitoring (MRM) was investigated as a quantitative analytical tool to complement precursor ion scanning. By monitoring specific parent/daughter ion transitions, selectivity and sensitivity can be maximized.

The development of quantitative analytical methods for NP and NPEs is somewhat hindered by the availability of pure standards. The majority of researchers in this field use standards, obtained from the manufacturers, which have been characterized using LC-UV detection and response factors derived through Beer's law. Gravimetrically prepared standards would produce more accurate results.



Technical Grade NP/NPEs Standards - GC-MS Traces

The environmental monitoring of NP and NPEs is being approached by developing a rapid flow injection (FIA)-MS/MS screening technique that would give a presence/absence of total NPEs above/below a specified guideline. Presence above the guideline would result in further speciation of NP and NPEs by quantitative LC-MS/MS and/or GC-MS/MS methods. This approach would eliminate the need for speciation of samples containing no NP and NPEs or when NP and NPEs are present below a specified guideline.

Results

A rapid LC - triple quadrupole mass spectrometer screening method for the detection of nonylphenol ethoxylates was developed using flow injection analysis (FIA) combined with atmospheric pressure ionisation (API) and mass analysis by precursor ion scanning and multiple reaction monitoring (MRM). Precursor ion scanning was used as a means of profiling NPEs. In the same experiment, MRM transitions were performed for all precursor ions ranging from $[EtO]_1$ - $[EtO]_{16}$. Precursor ion scans and MRM scans were combined in one experiment providing a quick semi-quantitative analytical tool. FIA-MS/MS allowed analysis times of < 60 seconds (conducive to a high throughput screening) with sample detection limits down to ~ 50 ng/L (ppt) total NPEs.

A quantitative normal phase LC-API (MRM) MS/MS method was developed to

complement the FIA-(precursor ion scanning/MRM) MS/MS screening method. The basic chromatography and instrument conditions have been developed. Fine tuning of the method, including ruggedness testing, is underway. Injecting over 100 sewage treatment plant sample extracts had no adverse affects on the performance of the LC-MS/MS system. LC-MS/MS traces were found to be interference free.

Sewage treatment plant (STP) samples, which had been submitted and characterized by GC-MS for extractable organics, were analysed using both the FIA-MS/MS and preliminary quantitative normal-phase LC-MS/MS analytical methods. NP and NPEs were detected in almost all influent, effluent and sludge (primary and digested) samples at concentrations between ng/L (ppt) and mg/L (ppm). NPEs were observed in samples in which no NPEs were detected by GC-MS characterization methods.

Current Status

A quantitative normal-phase LC-API (MRM) MS/MS method has been developed to complement the FIA-MS/MS screening method. Fine tuning of the normal-phase LC-API (MRM) MS/MS is being completed and the ruggedness of the entire method (wet preparation and instrument analysis) is to be evaluated. Initial work was done using technical grade NP and NPEs standards characterized and quantified by LC-UV. To produce more accurate results, pure nonylphenol and individual nonylphenol ethoxylate homologues are being isolated from technical mixtures using preparative column separation chromatography.

Publications and Presentations

Jeffry B. Plomley, Patrick W. Crozier and Vince Y. Taguchi. *The Characterization of Nonylphenol Ethoxylates in Sewage Treatment Plants by Combined Precursor Ion Scanning and Multiple Reaction Monitoring*. Journal of Chromatography A, 1999, Vol. 854, No. 1-2, 245-257.

B. Methods Development

Introduction

Much of the methods development effort this year was spent in completing projects initiated in the previous calendar year. An important new development is the method for dioxin-like PCBs, which was requested by a number of Laboratory Services Branch customers. The success of the new method was shown in an international round-robin, in which excellent results were generated compared to other leading laboratories. A significant effort was also spent in examining the Toxicity Characteristic Leaching Procedure (TCLP), in order to adapt TCLP for leach tests conducted under Ontario's hazardous waste regulation. The TCLP procedure, originally developed by the USEPA, is one of the most complex environmental analysis methods because of the wide range of volatile and non-volatile analytes of widely varying concentrations.

Methods for the determination of Polycyclic Aromatic Hydrocarbons (PAH) have been around for a long time, but the recent development of a wide range of stable-isotope (^{13}C) labelled standards has allowed the possibility of new methods with greatly improved precision and accuracy. Work on developing a new GC/MS method based on ^{13}C-labelled standards was started this year, and should be completed early in year 2000. Other new method development work concentrated on water applications. Methods for Aroclors and PCB congeners, taste and odour compounds, and total petroleum hydrocarbons (TPH) in water were also developed.

I. Large Volume Water Method for Aroclors and PCB Congeners

Study Leader:	Stephanie Lemanik, Applied Chromatography Section
Study Team:	Mary Wilson, Marilyn Pitcher, Paul Yang
Customer:	Environmental Monitoring and Reporting Branch (D.Boyd)

Objectives

To develop an analytical method for the analysis of polychlorinated biphenyl (PCB) congeners and Aroclors using large volume ambient water samples (16-litre), solid phase extraction, and GC/MS analysis at sub-ppt (part-per-trillion) detection limits to meet Ontario MOE's "Cleaner Water" Objective.

Background

The Laboratory Services Branch of the Ontario Ministry of the Environment has been analysing water samples for PCB congeners, including dioxin-like PCBs, and Aroclors using various analytical techniques at ppt and/or low ppb (part-per-trillion or part-per-billion) concentrations. A new and more sensitive method for the analysis of these environmental pollutants at low ppt concentrations was required for the *Great Lakes Monitoring and Assessment Program* of the Environmental Monitoring and Reporting Branch.

Results

A method for the analysis of 46 PCB congeners has been developed, validated, and audited by the Quality Management Office. The method met prescribed data quality objectives and has been used in a field study where more than 100 samples were analyzed. Customers has been trained to do the sample preparation so that samples can be prepared in the field, thus eliminating the problem of transporting large volume water samples from as far as Lake Superior back to the Resources Road laboratory. Working with the help of Nigel Cocks from Agilent Technology Canada, a program was developed for the calculation of concentrations of PCB congener groups

and total PCBs. Quality control and quality assurance (QC&QA) protocols have been enhanced by using a total of 13 deuterated internal standards representative of PCBs, polycyclic aromatic hydrocarbon (PAH), and organochlorine (OC) compound classes.

Current Status

In addition to the three types of PCB concentration data, this method is being validated for the determination of PAH and OC/CB target compounds. A final method analysing PAH, OC/CB and PCB will be submitted to the QM office for final approval.

II. Method for Dioxin-like PCBs in Environmental Samples

Study Leader:	K. MacPherson, Dioxins & Toxic Organics Section
Study Team:	T.Kolic, V.Khurana
Customer:	Environmental Monitoring and Reporting Branch (Fish Contaminants & Surface Water)

Objectives

To develop an isotope dilution method for the determination of congener specific PCBs. The World Health Organization (WHO) has assigned toxicity equivalency factors (TEFs) for 12 of the 209 possible PCB congeners. These compounds were assigned TEFs due to their demonstrated "dioxin-like" toxicological effects. These 12 congeners are collectively referred to as dioxin-like PCBs (DLPCBs).

Background

PCBs are all congeners of each other, because of their structural similarity. PCBs that have the same number of chorine atoms are called isomers. Only a few of the 209 PCBs are considered to be highly toxic, but because there are so many congeners, the determination of specific PCB isomers is difficult.

Studies have shown that 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2378-TCDD) and structurally related halogenated aromatic hydrocarbons (HAHs), invoke a number of common toxic responses mediated through a cystosolic receptor protein, the aryl hydrocarbon receptor (AhR). HAHs that act by binding to the AhR in vertebrates are reportedly accumulative in their toxicological effects and affect reproduction in organisms. Further studies have recognized that although 2,3,7,8-tcdd is the most toxic member of the HAHs, other compounds, sterically similar to 2378-tcdd, also cause similar effects but with varying potencies.

The Toxicity Equivalency Factors (TEF) scheme, as presented by the World Health Organization (WHO) identifies TEFs for 12 PCBs that exhibit dioxin-like toxicity (AhR mediated responses). In order to provide a more standardized assessment of toxicity the WHO developed a model where some dioxin, furan and dioxin-like PCB (DLPCB) congeners are assigned a toxicity factor, based on their relative toxicity to 2,3,7,8-TCDD. Although TEFs have not been derived for non-DLPCBs, it appears that at greater exposures these congeners may cause neuro-toxic effects. As well, the non-DLPCB congeners do not appear to act through the Ah receptor. To assess the toxic potential of environmental samples containing both dioxins/furans and PCBs, it was necessary to develop a method to distinguish the 12 PCB congeners for which TEFs have been assigned by WHO.

Results

The list of DLPCBs includes 4 coplanar (BZ#: 77, 81, 126, 169) and 8 mono-ortho congeners (BZ#:105, 114, 118, 123, 156, 157, 167 and 189). Approximately 5 g of sample were used. The samples were fortified with isotopically labeled standards (Wellington Laboratories, Guelph, Ont., Canada) prior to extraction. The coplanar PCB congeners were isolated with the dioxins and furans in a classical 3 column (silica/alumina/carbon) dioxin/furan cleanup method. The mono-ortho congeners elute before the dioxins and furans on the second (alumina) column. The method was developed to force polychlorinated diphenyl ethers (PCDPEs) into the mono-ortho PCB fraction, away from the dioxin/furan fraction. Soil sample extracts were chromatographed using a multi-layered acid/base/$AgNO_3$ impregnated silica column to remove bulk organic co-exctractables. Fractions collected at this stage were then chromatographed on a basic alumina column where some mono-ortho DLPCBs are collected in a fraction also containing the dioxins/furans. The remaining mono-ortho DLPCBs are collected in a separate fraction, which also contains some polychlorinated

diphenyl ether (PCDPE) compounds. PCDPEs interfere with polychlorinated dibenzofurans giving rise to biased high quantitative results for the furans, therefore a single fraction dioxin/furan/PCB method was not pursued.

Current Status

The method is complete for biota and soil/sediment samples. Method Detection Limits have been determined and are summarized in the table below. Future work planned involves modification of the method for other sample types including air, vegetation, and water. Fast GC with parallel column (2 columns, simultaneous injection) analysis will be investigated.

Method Detection Limits for DLPCBs in Fish

	MDL(PPT)	
IUPAC I.D.	**Fish**	**Soil/Sediment**
PCB 81	2	1.2
PCB 77	2.9	8.3
PCB 123	3.3	5
PCB 118	61	20
PCB 114	3.1	2.8
PCB 105	22	8.7
PCB 126	2.5	4.4
PCB 167	1.9	4.3
PCB 156	6	2.2
PCB 157	2.9	3.4
PCB 169	1.8	5.4
PCB 189	1	2.2

Based on the work reported here, a number of new methods incorporating dioxins, furans, and the DLPCBs have been adopted for varios sample types. The new

methods are listed in the following table.

TABLE 2 - DTO PRODUCTION METHODS

Method Code	Method Title
E3151B	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Soil and Sediment
E3122A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Ambient Air
E3164B	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCB in Groundwater and Aqueous Effluent
E3134A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Fish and Biota
E3163B	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Drinking Water
E3317A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Vegetation
E3318A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Precipitation
E3319A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Incinerator Emissions
E3320A	The Determination of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, and Dioxin-Like PCBs in Oil and Oil-Based Products

III. Method for the Determination of PAH in Soil, Sediment and Biota by Isotope Dilution GC-MS

Study Leader:	Adrienne Boden, Dioxin and Toxic Organics Section
Study Team:	Adrienne Boden, Mary Ann Bogard, Eric Reiner
Customer:	Standards Development Branch (Phytotoxicology), Region Operations Division and Environmental Monitoring and Reporting Branch (Surface Water Surveillance)

Objective

To develop an isotope dilution method for the determination of polycyclic aromatic hydrocarbons (PAH) in soil, sediment and biota. This new method will utilize isotopically-labelled analogues of the PAH of interest in order to compensate for: (i) variable recovery of PAH during sample pretreatment, and (ii) the effects of instrumental variables on PAH across the entire mass range.

Background

Polycyclic aromatic hydrocarbons are one of the largest single classes of chemical carcinogens known today. In order to quantitatively determine PAH in environmental samples, one must strive to achieve lower limits of detection while maintaining acceptable precision and accuracy levels. While the attainment of sensitivity and instrumental precision is quite easy using today's GC-MS instrumentation, the accuracy of quantitative data often suffers at the hand of sample losses during extraction, clean-up procedures and general sample handling in the laboratory.

Contrary to the current method, the isotope dilution method will intrinsically correct for sample losses during sample pretreatment procedures, thereby virtually eliminating errors due to poor recovery. In addition, 14 of the 16 priority PAH will be quantified using their own labelled analogue, significantly reducing errors due to varying chromatographic retention of different PAH and mass-related effects. The two remaining PAH will be quantified against their most structurally similar deuterated analogues. Overall, the new method will improve the accuracy of PAH data produced while maintaining the high productivity and rapid turnaround times of the former method.

Current Status

In preparation for the isotope dilution method, isotopically-labeled PAH standard stock solutions were prepared from solid standards. The standards to be used in this new method include 5 Calibration solutions, the Working Surrogate Standard Spiking Solution (containing 14 labeled PAH used for method recovery calculation), the d8-Naphthalene surrogate (used for sample blowdown recovery calculation), the d10-Anthracene surrogate (to be used for sample clean-up recovery calculation) and the Internal Standards working mixture. Preparation of a 4-year supply of the Working Surrogate Standard Spiking Solution and the other recovery surrogates and internal standards has been completed. Overall, 27 of the 32 standards planned for preparation are complete and the remaining 5 calibration standards are targeted for completion as soon as the standard mixtures involved are validated for concentration. These validations will be performed using external deuterated PAH cocktails purchased from Cambridge Isotope Labs. Performance data for the method validation will be produced for Standard Reference Materials and customer samples which have been previously analysed by our current methods. The method is targeted for completion by summer, 2000.

IV. Method for Taste and Odour Compounds in Water Using Ambersorb 572 and High Resolution Mass Spectrometry

Study Leader:	J-P.F.P. Palmentier, Mass Spectrometry Section
Study Team:	Vince Taguchi
Customer:	DWSP and drinking water customers (including Metro Works); MOE Regional Offices; County Regional Laboratories

Objective

To develop a general GC-HRMS method for taste and odour causing compounds by modifying the method for geosmin and 2-methylisoborneol (2-MIB) to incorporate 4 additional compounds: 2,3,6-trichloroanisole, 2,4,6-trichloroanisole, 2-isopropyl-3-methoxypyrazine and 2-isobutyl-3-methoxypyrazine.

Background

Taste and odour problems occur seasonally in drinking and surface waters around North America. Six compounds have been identified as being responsible for imparting earthy, musty taste and odour qualities to water, food and soil. These include geosmin, 2-methylisoborneol (2-MIB), 2,3,6-trichloroanisole (TCA), 2,4,6-TCA, 2-isopropyl-3-methoxypyrazine (IPMP) and 2-isobutyl-3-methoxypyrazine (IBMP). Geosmin and 2-MIB are semi-volatile metabolites of actinomycetes and blue-green algae and are most often responsible for taste and odour events. IPMP is another taste and odour causing compound resulting from actinomycetes activity in water and soil. IBMP has been found in food. 2,3,6-TCA and 2,4,6-TCA are formed from reactions occurring during chlorination of drinking water or are discharged in Kraft pulp mill effluent. Human threshold odour concentrations for these six compounds have been reported as 10 ng/L for geosmin, 29 ng/L for 2-MIB, 7-30 ng/L for 2,3,6-TCA, 2-5 ng/L for 2,4,6-TCA and 2 ng/L for both IPMP and IBMP. By modifying the LSB Ambersorb 572/GC-HRMS method for geosmin and 2-methylisoborneol (2-MIB) to incorporate the additional 4 compounds, a general method for taste and odour compounds with high productivity and rapid turnaround times would be available.

Results

Five of the six taste and odour compounds were within acceptable control limits for all spike levels (1 to 80 ng/L). The results for 2,3,6-TCA were consistently 35-50% lower than the expected values for all spiking solutions, which has been attributed to differences in recoveries between 2,3,6-TCA and 2,4,6-TCA from Ambersorb 572. Therefore, 2,3,6-TCA cannot be quantitated by isotope dilution using d_5-2,4,6-TCA with the present quantitation procedure. An alternative method of quantitation using an 8-point method recovery curve (from 1 ng/L to 96 ng/L) and interpolating between method recovery samples was instituted. The 2,3,6-TCA can now be quantitated using d_5-2,4,6-TCA as an internal standard. The new method (Method E3310) is on-line and available for routine sample analysis.

Current Status

Method development is complete (Method E3310). The method is on-line and producing routine sample data. An estimated 600 samples or more may be submitted yearly from the DWSP program. A paper for publication is currently being prepared for submission to a scientific journal.

Publications and Presentations

J-P Palmentier and Vince Taguchi, "The Determination of Six Taste and Odour Compounds in Water Using Ambersorb 572 and High Resolution Mass Spectrometry", presented at the 47th ASMS Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, U.S.A. , June 13th to June 17th, 1999.

V. Analytical Methods to Support the Toxicity Characteristic Leaching Procedure (TCLP)

Study Leader :	John Carron, Physical Chemistry & Litigation Section
Customer:	Standards Development Branch/Waste Management

Objectives

To provide the Branch with the capability to analyze leachates produced by using the EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP) for organic and inorganic parameters. This project investigated the use of the TCLP Zero Headspace Extractor for volatile organic compounds and evaluated the suitability of the current LSB analytical methods to analyze TCLP leachates for the new Schedule 4 parameter list in the proposed revision to Ontario Regulation 347.

Background

The Environmental Protection Act Regulation 347, states that "hazardous waste " means a waste that is a, *leachate toxic waste*. Two of the three proposed changes to this regulation include a "derived from" rule, and a new TCLP process and analysis of the leachate for an expanded list of organic and inorganic chemicals. The TCLP process proposed is identical to EPA method 1311. The expanded list of chemicals include many volatiles and semi volatiles such as pesticides and herbicides. If these new changes are implemented they will, make Ontario's hazardous waste regulation the toughest in the province's history, and they will be consistent with current rules set by the US EPA and provide clear information to the public, the handlers and the generators of hazardous waste.

Results

A request was made to several analytical suppliers for spiking solutions to address the chemicals and their concentrations. Standards were custom prepared by Protocol Analytical Supplies Inc. The large number of chemicals listed and the high concentration levels, necessitated that several different TCLP spiking solutions be

prepared. Enough organic spiking material was received in sealed glass ampoules, and in a bottle of custom made metals spiking solution, to do the present work and any follow up work.

Several waste samples were collected. They were analysed for bulk content in order to determine their suitability for leaching TCLP substances. The results demonstrated that these samples contained no significant levels of organic material, but did contain high levels of some TCLP metals. Three of these wastes were used to make a composite waste sample to provide sufficient waste material for leaching. Five of the samples containing the higher metal values were used to produce TCLP leachates. The leachate was sub divided into nine similar portions . Eight of the portions were spiked with different mixes of the TCLP metals and semi volatile organics at a mg/L toxic level. Five metals and six organics have been analysed. The data are currently being tabulated and reviewed. Suitability of the methods to analyse will be determined by the percent recovery of the spikes and precision of the analysis.

The concentration range of the TCLP volatiles was not suitable for demonstrating analytical performance for all the volatiles in one analysis. A different volatile spiking standard was made at a level similar to that being presently used in the laboratory providing waste analysis. This mixture was used for volatile standards and spikes. Ten volatile spikes in water, ten volatile spikes in waste leachate and fourteen spiked solid samples, extracted using the Zero Headspace Extractor (ZHE) were analysed using two different instruments. Analysis have been completed. A data comparison between the Headspace Capillary Gas Chromatography using Flame Ionisation Detection Electron Capture Detection (H/S-GC-FID/ECD) and Purge and Trap Capillary Gas Chromatography using Mass Spectrometry (P/T-GC-MSD), is being prepared.

The TCLP extraction procedure has been used on an in-house metal reference dust. Results will be compared to historical data that used the Ont. Reg . 347 leach extraction procedure. At the same time, three TCLP metals were spiked into water that was pH adjusted from low to high to demonstrate the low metal solubility at high pH. All analyses are complete. Data summary is in progress.

Current Status

Metal and volatile analyses are complete. Data are being tabulated and

evaluated for both. The analysis of pesticides in spiked leachates is in progress. A report for 85% of the spiking compounds is due at the end of March, 2000. LSB has no current method for Methyl Ethyl Ketone , Pyridine, Nitrobenzene, and Chloramines. Of the ninety three parameters, the following thirteen parameters have not been included in this study: Barium, Boron, Cyanazine, Cyanide, Diquat, Fluoride, Glyphosate, Nitrate+ Nitrite, NTA, Nitrite, Toxaphene, Vinyl chloride and Chlorinated Dioxins/Furans. Some additional work is expected for repeat analysis and a completed analytical process for TCLP extracts is targeted for the summer of 2000.

VI. Method for Total Petroleum Hydrocarbons (TPH) in Water

Study Leader:	Dave Morse, Physical Chemistry & Litigation Section
Customer:	Standards Development Branch

Objectives

To provide the Branch with the capability to analyse water for potential petroleum contamination, providing both quantitation and product identification.

Background

Petroleum hydrocarbon analysis has been performed by numerous techniques, primarily for the decommissioning of contaminated sites which have potable groundwater. The Laboratory Services Branch (LSB), in support of the recently published MOE document "Guidance on Sampling and Analytical Methods for Use at Contaminated Sites" is in the final stages of documentation for a technique which rapidly screens for petroleum hydrocarbons using a combination of headspace gas chromatography and liquid/liquid solvent extraction, followed by a combination of gas chromatography and gravimetric analysis. LSB is also in the final stages of documentation for a similar technique which will allow the identification of the type of petroleum contamination over an extended defined carbon range, C5 to C50, primarily

for spill situations. This technique also uses a combination of headspace gas chromatography and liquid/liquid solvent extraction, but is followed by high temperature gas chromatography.

Results

1. Determination of Petroleum Hydrocarbon in Water for the Decommissioning of Contaminated Sites.

This technique is divided into two groups, Light, C5 to C24, and Heavy, approximately C17 and greater. The Light group is further divided into total purgeables, C5 to C10, and extractables, C10+ to C24. Total purgeables are analysed by headspace gas chromatography, extractables are analysed by liquid/liquid extraction with hexane followed by silica separation and gas chromatography. The Light group recovery is approximately 80%, with a method detection limit of approximately 0.10 mg/L (ppm). The Heavy group is extracted by the same technique as the extractable portion of the Light group but is quantitated by gravimetric analysis. The recovery for the Heavy group is approximately 80% with a method detection limit of 1 mg/L (ppm).

2. Determination of Total Petroleum Hydrocarbon (C5 to C50) in Water.

For this method, total petroleum hydrocarbon (TPH) is defined as all petroleum hydrocarbons from n-pentane, C5 to n-pentacontane, C50. This hydrocarbon range is divided into three distillate ranges; light, C5 to C10 (ie. gasoline, naphtha), medium, C10 to C24 (ie. diesel, jet, home heating fuel) and heavy, C24 to C50 (ie. lubricating oil). TPH is analyzed similarly to the Light group described earlier in the "Determination of Petroleum Hydrocarbon in Water for the Decommissioning of Contaminated Sites", but the extractable range is extended to pentacontane by the use of high temperature gas chromatography. The recovery for the entire range of TPH is 80% with a method detection limit of 1 mg/L (ppm). This technique will allow the identification of the petroleum product throughout the stated carbon range.

Current Status

Final documentation for the new methods is being prepared for audit by the Quality Management Unit. It is expected that both methods will be available for use at LSB by the Spring, 2000.

C. Reference Centre Activities

In the 1998 R&D Report in this series, sections on *Collaborative Projects* and *Education & Training* were included. This year, these sections are replaced by this new section on *Reference Centre Activities*. The broader focus of this section is intended to capture the wide range of significant activities, in addition to collaborative projects with outside groups, that the Laboratory Services Branch performs.

I. Evaluation of GC Columns for Dioxin Determination

LSB Study Team:	Karen MacPherson, Tony Chen, Adrienne Boden, Eric Reiner, Dioxin & Toxic Organics Section
Collaboration with:	Restek Corporation, Bellefonte, P.A

The project was undertaken to develop analyte specific columns to be used in Fast GC applications. Retention times of organic compounds can be shortened by using narrower columns with thinner films, and by changing stationary phase formulations. The combination of analyte specific phases and Fast GC allows for the ultimate enhancement in chromatographic speed. For *Organochlorine Pesticides*, conventional analysis is carried out on DB-1, DB-5 and or DB-1701 30M 0.25mm, 0.25µm GC columns with run times of about 55 min. DTO evaluated analyte specific CLPesticides-1 and CLPesticides-2 30M 0.25mm, 0.25µm columns and determined that Fast GC could be used to significantly reduce analysis times. A method was developed using 20M 0.18mm, 0.18µm CLPesticides-1 and CLPesticides-2 GC columns with a run time of under 12 minutes. This Fast GC / analyte specific method has less co-elutions than the convention 55 minute method. Work was also done to study improved columns for *Dioxins / Furans, PCB and PAHs*. Preliminary experiments have been carried out to develop analyte specific columns for Dioxins / Furans, PCB and PAHs. The goal is to develop separate analyte specific Fast GC columns for Dioxins/Furans/DLPCBs, Congener PCBs and PAHs similar to the CLPesticides-1 and CLPesticides-2 columns used for OC Pesticide analysis.

II. Development of Environmental Reference Materials

LSB Study Team: Sathi Selliah (QMU), Eric Reiner (DTO)
Collaboration with: Maureen Leaver, CANMET

An Ontario Lake sediment was identified as a potential reference material when repeat analysis of dioxins and furans in this sample in 1994 showed extraordinary reproducibility of results. This sediment has excellent homogeneity and contains a very complex mixture of analytes at low concentrations. Analyte groups identified along with dioxins and furans include: PAHs, PCBs, metals, and a few organochlorine compounds. Because of these unique properties, this sediment was chosen as the first LSB candidate Certified Reference Material. This material, LSBRM9801, was physically processed by CANMET at their facilities in Ottawa. In an interlaboratory study to characterize it for Dioxins/Furans and dioxin-like PCBs, 36 laboratories from 17 countries registered, and results are expected by the first quarter, 2000. The large number of laboratories is expected to produce sufficient data to produce certified values for the 17 toxic dioxins/furans and 12 dioxin-like PCBs.

III. Mass Spectrometry Discussion Group

LSB Leader: Vince Taguchi
Collaboration with: Toronto Area Mass Spectrometry Discussion Group

For the past few years, the Laboratory Services Branch has been the site of the regular meetings of the *Toronto Area Mass Spectrometry Discussion Group*. Organized by Dr. Vince Taguchi, seven evening seminars were held during 1999 in the 125 Resources Road auditorium. The distinguished lineup of speakers and their topics of discussion were:

- Professor Michael Siu, York University. *The Biological Mass Spectrometry of Peptides and Proteins* [January 19].
- Professor Ray March, Trent University. *The Evolution of the New Water Quality Centre at Trent University: From Ion Trap to ESI/Q/TOF* [February 23].
- Jerry Hart, Micromass UK Ltd. *AutoSpec-NT: A New Era in High Resolution Mass Spectrometry* [May 20].
- Professor John Allison, Michigan State University. *Better Mass Spectrometry Through Chemistry* [September 15].

- Dr. Vladimir Kovacik, Slovak Academy of Sciences. *The Use of Adduct Ions in the Structure Elucidation of Complex Saccharides* [September 29].
- Professor Jack Miller, Brock University. *Thirty-five Years of Mass Spectrometry of Organometallic and Coordination Compounds* [October 19].
- Ray Matejczyk, Leco Corporation. *Fast Data Acquisition for GC-MS and LC-MS* [November 2].

For notices of upcoming seminars, those interested should check the internet site *www.csms.inter.ab.ca*.

IV. Total Petroleum Hydrocarbon (TPH) National Guideline

LSB Leader:	George Kanert & Dave Morse, Physical Chemistry & Litigation Section
Collaboration with:	Canadian Council of Ministers of the Environment (CCME)

For many years, laboratories and regulators have struggled with the issue of how to measure TPH pollution. Because various laboratories employed different methods for this determination, TPH concentrations could not be compared on the same basis; in fact, there was no universal definition of what exactly TPH was. Under the direction of the CCME, the major stakeholders in Canada have been working for more than a year on harmonizing the definition of TPH, and on developing a recommended method for TPH determination. George Kanert and Dave Morse of the MOE – Laboratory Services Branch have provided leadership to achieve these objectives.

D. LSB Seminar Series

After five years of the seminar series, this past year proved to be significant in the much greater numbers of non-LSB attendees for most seminars. This fits with the expanded reference centre emphasis of LSB, as topical seminars are a service to the entire Ontario environmental analytical community. Brief descriptions of the seminars held are given below.

I. Solid Phase Extraction Technology; Michael F. Burke (University of Arizona) and Richard Calverley (International Sorbent Technology)

In partnership with Chromatographic Specialties Inc., this seminar was presented April 19 to over 50 attendees. After describing the general principles and theory of Solid Phase Extraction (SPE), the speakers discussed the nature of molecular interactions in SPE, and how to use this knowledge to conduct efficient method development. They then described recent developments in environmental analysis.

II. GC Method Development and Techniques; Tips & Tricks of Troubleshooting Capillary GC Systems: J&W Seminar [hosted by MOE-LSB and Chromatographic Specialties Inc.]

This seminar was a combination of two modules. The *GC Method Development* module described, with practical examples, how to set up a GC analysis method to give optimized chromatographic results. Decisions on choice of injection techniques & optimization, and carrier gas & oven temperature program optimization were described. In the *Tips & Tricks* portion of the seminar, common problems and their causes – and diagnostic tests for troubleshooting – were demonstrated. Over 80 LSB and external staff attended this seminar May 10.

III. Analysis of Pesticides, Endocrine Disruptors, Nutraceuticals and Related Compounds Using HPLC and GC/MS

A specialist from Waters Corporation presented this seminar July 22 to some 40 attendees. Principal focus of the seminar was how recent advances in solvent delivery, interface technology, sample preparation, and column chemistry make LC/MS a powerful tool for environmental, natural product, and food chemists. With the proliferation of affordable, bench-top systems and much improved detection limits, the technique of LC/MS has become a mainstream tool for many environmental applications.

IV. Jones Chromatography Seminar on HPLC (sponsored by Chromatographic Specialties Inc.)

Neil Herbert of Jones Chromatography presented a wide-ranging half-day seminar on HPLC September 29 to some 50 attendees. Topics covered included selection of columns and media, factors affecting HPLC performance, optimized columns for LC-MS and rapid LC, and method development and assay validation. The use of column switching devices was highlighted.

V. Optimization of HPLC Systems, Jim Whitford (Valco Corp.)

Previous seminars also discussed HPLC optimization, but this one was more like an interactive tutorial aimed at a small group (6) of hands-on HPLC users. This seminar format allowed attendees the opportunity to discuss their specific HPLC issues in the areas of solvent delivery selection, detector selection, and fittings & tubing. The smaller group of knowledgeable HPLC users also allowed Jim Whitford to deliver the November 10 seminar at a higher technical level than is possible in a general seminar presented to a larger group of attendees who have widely varying HPLC experience.

VI. New Developments in the Determination of Dioxins and Other Persistent Organic Pollutants, Karen MacPherson, Laboratory Services Branch

Dioxins and related classes of toxic pollutants fall into a group of chemicals collectively called *endocrine disruptors*, because of their demonstrated effects in biological systems. Although human exposures to high concentrations of these compounds are certainly harmful, little is understood about the effects of long-term exposure to background levels. Analytical technologies for these compounds are generally expensive and relatively slow, but can achieve very low detection limits. About 80 seminar attendees on Nov. 10 learned how newer technologies such as Fast GC and Time-of-Flight Mass Spectrometry are being used to enhance our ability to measure low concentrations of endocrine disruptor compounds in the environment.

VI. Future Laboratory Technologies, Stuart Cram, Agilent Technologies

About 50 attendees heard on November 17 what laboratory technologies are "just around the corner". New developments in silicon-based technology will allow the handling of sample volumes much smaller than are common in today's routine testing laboratory. This will lead to huge improvements in detection limits, speed of analysis, and reproducibility. Computer technologies will make it possible for the analyst to control field sampling and analysis variables from a remote location.

VII. Advances in GC Column Technologies & Applications, and Rapid Resolution Liquid Cromatography, Steve Hutt and Brian Smith, Agilent Technologies

In the first part of this seminar December 16, close to 40 attendees were shown how advances in column deactivation technologies are leading to improved peak shape, resolution, and detection limits for acidic, basic, polar, and other compound types. Stationary phase advances include improved thermal stability, reduction of bleed, reductions in minimum operating temperatures, greater solvent and sample compatibility and improved resolution. Those present also learned the considerations and practicalities of rapid resolution chromatography (RRC) for liquid chromatography. In RRC, the objective is not to achieve the optimum resolution, but to achieve sufficient resolution of components in the shortest possible time by reducing column dimensions, possibly combined with increased flow rate and reduced particle size.

Publications, Presentations and Methods Laboratory Services Branch

A. Publications

1. K.A. MacPherson, R. Brunato, T. Chen, M.A. Bogard and E.J. Reiner. Optimization of Gas Chromatographic Parameters for Reduced Analysis Times of Chlorinated Organic Compounds. *Organohalogen Compounds* **1999**, *40*, 19-22.

2. Karen A. MacPherson, Terry M. Kolic, V. Khurana and Eric J. Reiner. Method for Congener-Specific Determination of Dioxin-Like PCBs in Biota and Soil/Sediments. *Organohalogen Compounds* **1999**, *40*, 193-196.

3. Jeffry B. Plomley, Patrick W. Crozier and Vince Y. Taguchi. Characterization of Nonyl Phenol Ethoxylates in Sewage Treatment Plants by Combined Precursor Ion Scanning and Multiple Reaction Monitoring. *J. Chromatogr. A* **1999**, *854*, 245-257.

4. Vince Taguchi. Back to Basics. *Laboratory Gazette* December **1999**, 12-13.

5. Sylvia Cussion. Interlaboratory Study 96-3: Polycyclic Aromatic Hydrocarbons (PAHs) in Large Volume Stormwater Samples. *Ontario Ministry of Environment, Laboratory Services Branch Report*, August **1999**, 9pp.

6. Ray E. Clement, Paul W. Yang, and Carolyn J. Koester. Environmental Analysis. *Anal. Chem.* **1999**, *71*, 257R-292R.

7. Ray Clement. Eye Surgery as Seen More Clearly by Ray Clement. *Crucible* **1999**, *31*, 11-14.

B. Presentations

1. *Ray Clement*. Ministry of Environment Partners in Air Program. Presented at the *Ontario Society for Environmental Education Annual Conference*, Paradise Lake (Waterloo), May 2, **1999.**

2. *Ray Clement*. Trends in Environmental Analysis. Presented at the *National Symposium on Analytical Chemistry and Spectroscopy: New Trends in Chemical Analysis*, Toronto, May 14, **1999.**

3. *Lorna Grey*, P. Yang and B. Nguyen. Determi *31st* nation of Paraquat and Diquat Levels in Soil and Vegetation Samples. Presented at the *31st Eastern Canada Pesticide and Environmental Contaminants Workshop*, Niagara-on-the-Lake, May 18, **1999**.

4. *Patrick Crozier*, Jeffry Plomley and Larry Matchuk. Pushing the Limits of Detection: The Trace Level Determination of Polycyclic Aromatic Hydrocarbons in Waters Using Ion Trap Mass Spectrometry. Presented at the *31st Eastern Canada Pesticide and Environmental Contaminants Workshop*, Niagara-on-the-Lake, May 18, **1999.**

5. *Lorna Grey*, P. Yang, B. Nguyen, P. Cheung and P. Lachmaniuk. The Determination of Glyphosate in Soil, Vegetation and Water Matrices Using LC-MSD. Presented at the *31st Eastern Canada Pesticide and Environmental Contaminants Workshop*, Niagara-on-the-Lake, May 19, **1999.**

6. *Tony Chen*, Maryann Bogard and Eric Reiner. The Determination of Organochlorine Pesticides (OCs) in Environmental Samples Using Fast GC. Presented at the *31st Eastern Canada Pesticide and Environmental Contaminants Workshop*, Niagara-on-the-Lake, May 19, **1999.**

7. *J.-P. Palmentier* and V.Y. Taguchi. The Determination of Six Taste and Odour Compounds in Water using Ambersorb 572 and High Resolution Mass Spectrometry. Poster presented at the *American Society for Mass Spectrometry Conference*, Dallas, Texas, June 17, **1999.**

8. *K.A. MacPherson*, R. Brunato, T. Chen, M.A. Bogard and E.J. Reiner. Optimization of Gas Chromatographic Parameters for Reduced Analysis Times of Chlorinated Organic Compounds. Presented at the *19th International Symposium on Halogenated Environmental Organic Pollutants and POPs*, Venice, Italy, September 13, **1999**.

9. *Karen A. MacPherson*, Terry M. Kolic, V. Khurana and Eric J. Reiner. Method for Congener-Specific Determination of Dioxin-Like PCBs in Biota and Soil/Sediments. Presented at the *19th International Symposium on Halogenated Environmental Organic Pollutants and POPs*, Venice, Italy, September 13, **1999**.

10. *Mark Powell*. Development of a Method for Trace Metals in Fish Tissue Using ICP-MS. Presented at the *26th Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS)*, Vancouver, October **1999**.

11. Ray Clement. Why Chemistry is Important to Environmental Science. Invited lecture presented to 1st year *York University* students, Nov. 1, **1999.**

12. Ray Clement. The Importance of Science to Policy Making. Invited lecture presented to 4th year *York University* students, Nov. 8, **1999.**

13. Ray Clement. Environmental Analysis in the Real World. Invited lecture presented to 2nd year *University of Waterloo* analytical chemistry students, November 24, **1999.**

C. New Laboratory Services Branch Analytical Methods

1. Method E3407: *Membrane Filtration Method Using DC Agar for the Simultaneous Detection and Enumeration of Total Coliforms and Eschericia Coli* [contact Rhonda Schop]

2. Method E3408: *The Spread Plate Procedure for the Enumeration of Aerobic Heterotrophic Bacteria in Drinking Water* [contact Rhonda Schop]

3. Method E3409: *The Determination of Trace Metals in Air by Moss Bag Collection and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)* [contact Mark Powell]

4. Method E3411: *The Determination of Polychlorinated Biphenyl Congeners (PCBs) in Fish, Clams and Mussels by Gas Liquid Chromatography - Electron Capture Detection (GC - ECD)* [contact Robert Brunato]

5. Method E3415: *The Determination of Glyphosate in Water and Vegetation by HPLC-Electrospray Ionisation MS* [contact Lorna Grey]

6. Method E3417: *The Determination of Diquat and Paraquat in Water, Soil and Vegetation by HPLC-Photodiode Array and/or Electrospray Ionisation MS* [contact Lorna Grey]

7. Method E3310: *The Determination of Taste and Odour Compounds in Water by GC-HRMS* [contact Jean-Paul Palmentier]

8. Method E3402A: *The Determination of Metals in Air Particulates by Acid Digestion and ICP-MS* [contact Mark Powell]